SUPPORTED IONIC LIQUID AND THE USE THEREOF IN THE DISPROPORTIONATION OF ISOPENTANE

Background of the Invention

The invention relates to catalyst systems useful in hydrocarbon upgrading processes and to methods for their use. In another aspect, this invention relates to processes for the disproportionation of a C_5 paraffin.

It is known that ionic liquids can be used in various hydrocarbon conversion processes. However, we have found an ionic liquid dispersed on a support having an average pore diameter greater than about 225 angstroms is unexpectedly effective at disproportionating isopentane.

SUMMARY OF THE INVENTION

It is an object of this invention to provide an improved supported ionic liquid which when used in the disproportionation of a C_5 paraffin results in increased product formation.

Another object of this invention is to provide an improved process for the disproportionation of a C_5 paraffin in which the yield of disproportionation products is increased.

The inventive catalyst system comprises an ionic liquid dispersed on a support having an average pore diameter greater than about 225 angstroms. The inventive catalyst system can be used in the disproportionation of a C_5 paraffin by contacting a C_5 paraffin, under conversion conditions, with the inventive catalyst system.

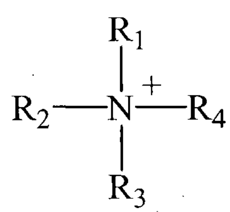
Other objects and advantages of the invention will become apparent from the detailed description and the appended claims.

Detailed Description of the Invention

The hydrocarbon feed stream of the process of this invention can be any hydrocarbon-containing mixture that comprises at least one C_5 paraffin such as n-pentane, 2-methylbutane, neopentane, or mixtures thereof, and an initiator selected from the group consisting of an olefin, alkyl halides, and combinations thereof. The olefin or alkyl halide preferably has in the range of from 2 to 20 carbon atoms per molecule, more preferably has in the range of from 3 to 6 carbon atoms per molecule, and most preferably has in the range of from 4 to 5 carbon atoms per molecule. Generally, the feed contains more than about 50 weight-percent C_5 paraffin, preferably about 60-100 weight percent C_5 paraffin, and more preferably about 75 - 90 weight percent C_5 paraffin. The feed can contain other hydrocarbons that do not interfere with the process of this invention, i.e. minor amounts of other alkanes, such as n-butane, isobutane, n-hexane and the like, and alkenes (monoolefins).

The inventive catalyst system comprises, consists of, or consists essentially of an ionic liquid dispersed on a support having an average pore diameter greater than about 225 angstroms, preferably greater than about 250 angstroms, and more preferably greater than about 275 angstroms. The support preferably has a surface area less than about 700 m^2 per gram and is preferably non-crystalline. The support is most preferably a silica.

The ionic liquid comprises, consists of, or consists essentially of a cation and an anion. The cation is preferably selected from the group consisting of ions defined by the formulas:



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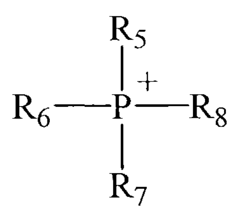

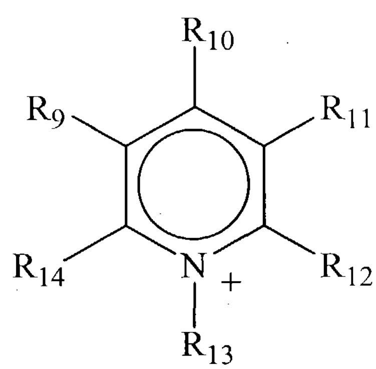

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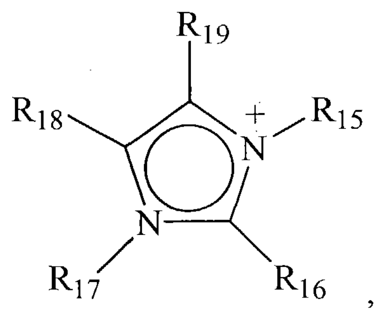

and combinations of any two or more thereof, wherein:

R_1, R_2, R_3, R_5, R_6 and R_7 are selected from saturated and unsaturated hydrocarbons containing from 1 to 7 carbon atoms per molecule;

R_4, R_8, R_9, R_{10}, R_{11}, R_{12}, R_{13}, R_{14}, R_{15}, R_{16}, R_{17}, R_{18} and R_{19} are selected from saturated and unsaturated hydrocarbons containing from 1 to 7 carbon atoms per molecule, and hydrogen.

The anion is selected from the group consisting of halides of: Group IIIA metals, copper, zinc, iron, phosphorus and combinations thereof. More preferably, the anion is selected from the group consisting of chlorides of aluminum, gallium, copper, zinc, and iron; fluorides of phosphorus and boron, and combinations thereof.

The ionic liquid preferably has the general formula $R_1\ R_2\ R_3\ N\ H^+\ Al_n\ Cl_{3n+1}^-$, wherein n = 1, 2, or 3; and more preferably has the general formula $(CH_3)_3\ N\ H^+ Al_2\ Cl_7^-$.

The inventive process comprises, consists of, or consists essentially of, a) contacting, under conversion conditions, the hydrocarbon feed stream with the inventive catalyst system; and b) withdrawing a product stream

comprising a C_4 paraffin which is preferably isobutane and at least one C_6 paraffin which is preferably a hexane isomer.

The conversion conditions include a temperature in the range of from about 100°F to about 1000°F, preferably in the range of from about 140°F to about 250°F, and more preferably in the range of from about 150°F to about 220°F.

The following examples are presented to further illustrate this invention and are not to be construed as unduly limiting its scope.

EXAMPLE I

For Inventive Run 1, 7.38 grams of $AlCl_3$ were mixed with 2.71 grams of trimethylammonium chloride ($N(CH_3)_3$:HCl) (at approximately 2 equivalents $AlCl_3$ and 1 equivalent ($N(CH_3)_3$:HCl)) to form an ionic liquid. A 1.98 gram quantity of silica spheres, having a surface area greater than about 400 m^2/g, a pore volume of 3.0 cc/g, and an average pore diameter of 308Å, were added to the ionic liquid along with 17.01 grams of the inert support Alundum alumina to form a mixture. The mixture was then charged to a reactor.

An isopentane feed was charged to the reactor at varying reactor temperatures and liquid hourly space velocities. Results of such are presented in Table 1.

Table I

TOS, Hrs	Feed	1	2	3	4	5	6	7	8
Rx Temp, °F		102.7	102.0	140.5	151.3	199.2	201.9	201.3	201.4
LHSV, hr-1		4	2	2	2	2	2	2	2
Component	Wt%	Wt%	Wt%	Wt%	Wt%	Wt%	Wt%	Wt%	Wt%
C3	0.000	0.000	0.000	0.000	0.011	0.112	0.266	0.174	0.127
iC4	0.057	2.851	3.494	4.425	16.507	32.702	33.686	28.550	24.162
NC4	0.000	0.084	0.086	0.088	0.251	1.346	2.174	1.279	0.870
NeoC5	0.198	0.192	0.192	0.193	0.195	0.199	0.198	0.195	0.194
iC5	97.070	88.936	87.389	85.682	58.319	29.846	27.090	32.806	41.167
NC5	0.421	0.616	0.704	0.905	2.897	4.884	5.026	4.194	3.417
C5=	2.166	0.016	0.268	0.016	0.027	0.020	0.019	0.037	0.023
Unk C3-C5	0.087	0.000	0.010	0.000	0.002	0.000	0.001	0.001	0.013
22DMC4	0.000	0.010	0.016	0.027	0.606	2.000	1.860	0.994	0.619
23DMC4	0.000	0.396	0.495	0.690	2.142	2.682	2.629	3.085	3.060
2MC5	0.000	1.338	1.605	2.124	5.804	7.168	7.250	8.608	8.689
3MC5	0.000	0.625	0.750	0.994	2.874	3.658	3.836	4.587	4.642
NC6	0.000	0.013	0.018	0.027	0.461	1.327	1.611	1.201	0.816
Unk C6	0.000	0.001	0.017	0.000	0.000	0.016	0.015	0.025	0.014
Total C6 Par.	0.000	2.382	2.883	3.862	11.886	16.834	17.186	18.475	17.826
C7+	0.000	4.923	4.956	4.830	9.905	14.043	14.339	14.263	12.187
Total	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000
Moles C4		0.050	0.062	0.078	0.288	0.586	0.617	0.513	0.431
Moles C6		0.028	0.033	0.045	0.138	0.195	0.199	0.214	0.207
iC5 Conv.		8.38	9.97	11.73	39.92	69.25	72.09	66.20	57.59

The data in Table I demonstrate that a catalyst system including an ionic liquid dispersed on silica spheres having an average pore diameter greater than about 225Å (specifically, 308Å) results in significant isopentane conversion, with even higher conversions at reactor temperatures in excess of 150°F.

For Runs 2 through 5, the catalysts were made from about 2 equivalents $AlCl_3$ and about 1 equivalent $N(CH_3)_3$:HCl to generate an ionic

liquid to which silica supports were added, as shown in Table II. An isopentane feed comprising about 98.2 – 98.4 wt. % isopentane, about 0.8 - 1.4 wt. % $C_5 =$; ~ 0.2 wt. % neo $C_5 =$ and about 0.13 – 0.15 wt. % C_4 paraffins, was charged to each reactor at an LHSV of 2 $hr.^{-1}$. Results of the conversions are presented in Table II.

Table II.

Silica Support	A[1]	B_1[2]	B_2[2]	B_3[2]
Surface Area, m2/g	269	321	403	537
Ave Pore Diam, Angstroms	164	372	308	228
Ave Pore Vol, cc/g	1.1	2.98	3.10	3.06
Rx Temp, °F	229.0	200.0	201.9	200.7
IC5 Conversion, wt.%	30.5	76.0	72.2	53.5
1 A = Davison G-57 grade 2 B = Silica microspheres from Philadelphia Quartz				

The data in Table II demonstrate that ionic liquid catalyst systems which have silica supports with higher average pore diameters result in higher isopentane conversion as compared to ionic liquid catalyst systems which have lower average pore diameter silica supports.

For Inventive Run 6, 2.19 grams of $N(CH_3)_3$:HCl were added to 7.92 grams of $GaCl_3$ to form an ionic liquid. A 2.05 gram quantity of silica spheres, having a surface area greater than about 400 m^2/g, a pore volume of 3.0 cc/g, and an average pore diameter of 308Å , were added to the ionic liquid along with 17.94 grams of Alundum alumina to form a mixture. The mixture was then charged to a reactor. An isopentane feed, as shown in Table III, was charged to the reactor. Results of such are presented in Table III.

Table III.

g catalyst	12.16				
mL Catalyst	12.5				
H2 Rate, sccm	0	0	0	0	0
Feed Rate, mL/hr	25	25	25	25	25
LHSV, hr-1	--	2	2	2	2
Rx Temp, °F	193.3	202.5	204.0	203.4	202.4
TOS, hrs.	Feed	2	3	4	5
C3	0	0.050	0.047	0.035	0.028
iC4	0.057	17.014	17.294	16.137	15.275
nC4	0	0.274	0.261	0.227	0.206
NeoC5	0.198	0.199	0.201	0.200	0.199
iC5	97.07	54.220	54.221	56.733	58.573
nC5	0.421	1.837	1.823	1.693	1.591
C5=	2.166	0	0	0	0
UNK $C_3 - C_5$	0.087	0.039	0.041	0.046	0.052
22DMC4	--	0.165	0.157	0.123	0.099
23DMC4	--	3.328	3.348	3.188	3.050
2MC5	--	10.622	10.654	10.369	10.172
3MC5	--	5.695	5.709	5.562	5.457
nC6	--	0.320	0.312	0.262	0.225
UNK C6	--	0	0.013	0.020	0.022
Total C6 Paraffin	--	20.170	20.193	19.524	19.025
C7+	--	6.197	5.920	5.404	5.051
TOTAL	100.00	100	100	100	100
IC_5 Conversion	--	44.1	44.1	41.6	39.7